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Thermodynamic ground states of platinum metal nitrides

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We have systematically studied the thermodynamic stabilities of various phases of the nitrides of the platinum metal elements using density functional theory. We show that for the nitrides of Rh, Pd, Ir and Pt two new crystal structures, in which the metal ions occupy simple tetragonal lattice sites, have lower formation enthalpies at ambient conditions than any previously proposed structures. The region of stability can extend up to 17 GPa for PtN₂. Furthermore, we show that according to calculations using the local density approximation, these new compounds are also thermodynamically stable at ambient pressure and thus may be the ground state phases for these materials. We further discuss the fact that the local density and generalized gradient approximations predict different values of the absolute formation enthalpies as well different relative stabilities between simple tetragonal and the pyrite or marcasite structures.

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Until recently none of the Platinum-Metal (PM) elements (Pt, Ir, Os, Ru, Rh, Pd) were known to form stable compounds with nitrogen. Several such compounds have now been synthesized primarily under conditions of high static pressure and temperature (in the range of 60 GPa and 2000K respectively) [1]. These include nitrides of Pt [2, 3], Ir [3, 4], Os [4] and Pd [5]. Except for PdN₂ all these compounds have been shown to be at least metastable at ambient conditions. The resulting crystal structures have been investigated by several groups both experimentally and theoretically [2–8], and by now consensus has been reached concerning the observed crystal structures and stoichiometry (one metal atom for every nitrogen dimer). PtN₂ and PdN₂ are formed in the pyrite crystal structure, a cubic phase with the metal atoms occupying fcc sites. The nitrogen dimers are centered around the fcc octahedral interstitial sites, oriented in all the four possible $\langle 111 \rangle$ directions, such that all the nearest neighbor dimers make an angle of 70.53° with each other. A rotation of dimers such that two pairs point in the $[111]$ and $[\bar{1}\bar{1}\bar{1}]$ direction, respectively, results in the marcasite structure, the predicted ground state phase of RuN₂, RhN₂ and OsN₂ [7]. A small lattice distortion of marcasite then yields the monoclinic baddeleyite (CoSb₂) structure found in IrN₂ [5, 7].

The low-pressure phase diagrams of these systems are still not well understood. In particular their degree of thermodynamic stability has only been addressed briefly [3], where it was proposed that the Pt-N compound is only metastable at low pressures. In this work, we address this issue by calculating the formation enthalpies of all the PM nitrides as a function of pressure. We also report the discovery of two new low-energy crystal structures that at low pressures are thermodynamically more stable than any of the crystal phases that have up to now been synthesized experimentally or calculated from the-

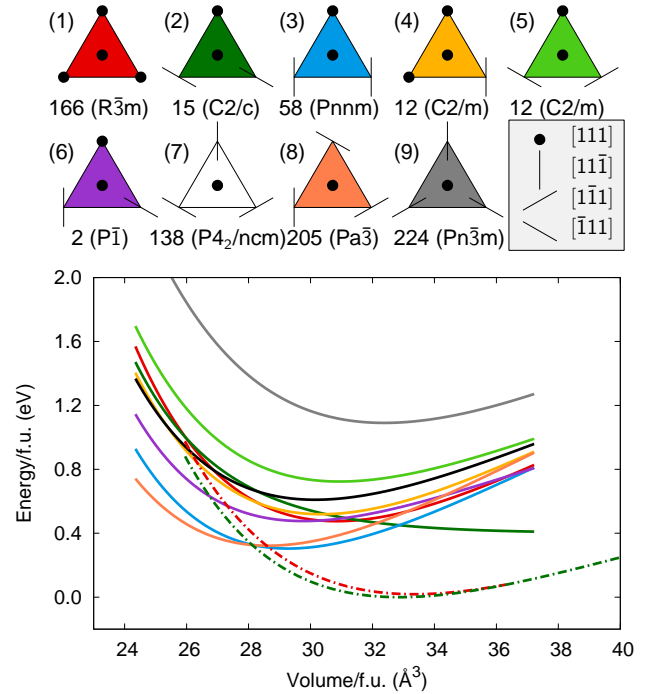


FIG. 1: (Color online) Top: Projections of all possible distinct nitrogen dimer orientations derived from the 12-atom conventional unit cell, along with the space group number and Hermann-Mauguin symbol of the corresponding structure. Bottom: Energy vs. volume curves from LDA for the above relaxed structures (solid lines) in the case of PdN₂. Each structure can be identified by matching the line color to the corresponding triangle color. Note that structure 7 corresponds to the black line. The green and red dashed lines correspond to the ST_{AA} and ST_{AB} structures, respectively.

ory. To our knowledge, these new crystalline phases have not previously been observed in any other compound.

In spite of the apparent differences in the overall symmetries of the pyrite, marcasite and baddeleyite structures, they all belong to the same class of crystal structures. They can be obtained by placing the PM atoms on an fcc lattice and the center of $\langle 111 \rangle$ -oriented nitrogen dimers on the octahedral interstitial sites of this lattice and allowing for atomic relaxations. For each nitrogen dimer there are four possible orientations, and thus for crystals with the periodicity of the fcc unit cell having four distinct PM-N₂ units, there are nine different crystal structures, two of which are the pyrite and marcasite phases. Note that as mentioned above, the baddeleyite structure is merely a distorted marcasite structure.

Geometrically each individual crystal structure in this class can be distinguished by the projections of its dimers centered at $0.5a\hat{x}$, $0.5a\hat{y}$, $0.5a\hat{z}$ and $0.5a(\hat{x} + \hat{y} + \hat{z})$ onto a $\langle 111 \rangle$ -plane. The dimer projections and space groups of the resulting crystal phases are displayed in the top panel of Fig. 1. For reference, structures (3) and (8) correspond to marcasite and pyrite, respectively. To assess their theoretical equation-of-state we have performed density functional theory calculations using projector augmented-waves as implemented in the Vienna ab-initio simulation package [9]. Both atomic position and cell shape relaxations were performed. In fact, only structures (8) and (9) maintained cubic symmetry after relaxation, while the others showed deviations of various magnitude. The resulting LDA energy vs volume curves for PdN₂ are shown as the solid lines in the lower panel of Fig. 1. As expected, amongst these structures, pyrite and marcasite have the lowest energies in the low-pressure region.

Besides the nine structures mentioned above, we also show in Fig. 1 the corresponding curves for two additional structures (dashed lines). These are obtained by a continuous transformation from structure (2) by translating every other (001) plane in the $[100]$ direction (corresponding to a zone-boundary phonon mode). By allowing the lattice to relax by a tetragonal distortion in the $[001]$ direction, the metal ions become arranged in a simple tetragonal (ST) lattice. During this transformation the nitrogen dimers that initially were oriented in the $\langle 111 \rangle$ directions collapse into the (001) planes and now point in the $\langle 100 \rangle$ and $\langle 001 \rangle$ directions. In this way, a new class of crystal structures is created where metal nitride layers are stacked in different sequences. Each layer is composed of metal ions occupying square lattice sites and face-centered nitrogen dimers pointing along the edges of the squares and always being perpendicular to the four nearest-neighbor dimers. Fig. 2 illustrates two particularly high-symmetry structures in this class with AA and AB stacking that have lower energies than any previously proposed crystal structure for most PM nitrides at ambient conditions. The first structure, hereafter denoted ST_{AA}, is simple tetragonal and belongs to space group 127 (P4/mbm). The metal ions occupy the 2a Wyck-

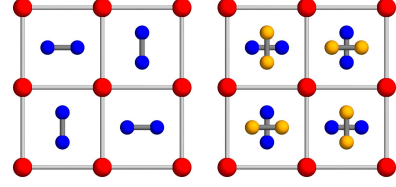


FIG. 2: (Color online) Conventional unit cells of ST_{AA} (left) and ST_{AB} (right) viewed along the c -axis. Red, blue and yellow spheres represent metal ions, nitrogens in layer A and nitrogens in layer B, respectively.

off positions and the nitrogen atoms are located at the 4g positions. The second structure, ST_{AB}, is monoclinic and belongs to space group 12 ($P2_1/m$). The metal ions occupy the 4e sites and the nitrogen atoms are located at the 4h and 4i positions.

As is clearly seen in Fig. 1, the ST structures at low pressures are significantly lower in energy than both the pyrite and marcasite structures. Also, their equilibrium volumes are shifted towards larger volumes and the bulk moduli are smaller. Both LDA and GGA calculations yield small but finite densities-of-states at the Fermi level for the ST structures [11]. However, it is well-known that these approximations often underestimate band gaps and e.g. predict Ge to be a metal. Hence, it is quite possible that the ST phases can be insulators with small band gaps.

The high-pressure PM-nitride synthesis results from the past few years have established the extent of (meta-)stability of many of these compounds. Since they have not been observed in nature, it is reasonable to rule out that they are thermodynamically stable with respect to phase separation at ambient pressure and temperature conditions. Based on experiments it is known that they are certainly stable at pressures above 50 GPa, and that PtN₂ (pyrite), IrN₂ (baddeleyite) and OsN₂ (marcasite), are at least metastable at zero pressure.

There is however no real understanding either of the relative stabilities among the compounds or of their degree of metastability at low-pressure conditions. These are very important issues for the synthesis and potential application of these materials. As it is yet difficult to assess their equilibrium phase diagrams experimentally we have performed extensive first principles calculations of the thermodynamic stabilities of the six PMN₂ compounds as a function of pressure.

The thermodynamic stability of any PMN₂ compound with respect to the separate phases as a function of pressure, is quantified in terms of the formation enthalpy:

$$\Delta H = H_{\text{PMN}_2} - H_{\text{PM}} - H_{\text{N}_2}$$

Under experimental conditions, nitrogen is molecular in its solid phase. At ambient pressure, it crystallizes into a hexagonal phase only at low temperatures and exhibits

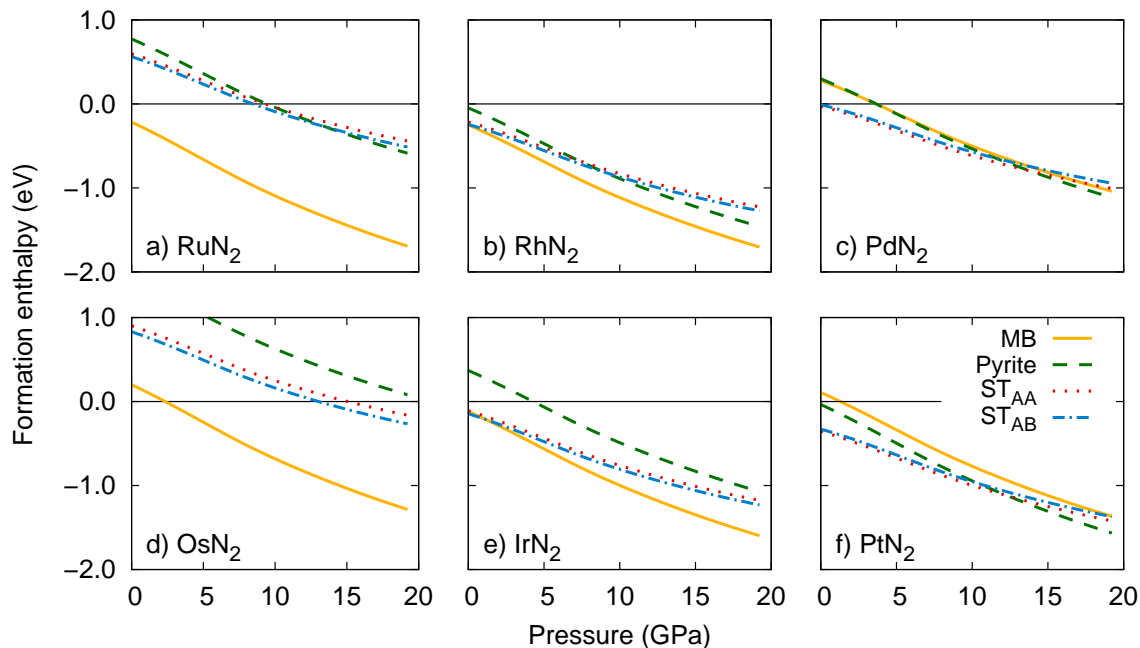


FIG. 3: LDA Formation enthalpies of a) RuN₂, b) RhN₂, c) PdN₂, d) OsN₂, e) IrN₂ and f) PtN₂ as a function of pressure for marcasite or baddeleyite (MB), pyrite and the two simple tetragonal structures.

a polymorphic phase diagram undergoing several structural transformations upon increasing pressure. It is thus quite difficult to perform accurate free energy calculations for this system. Therefore, the most reliable way of estimating the enthalpy of this system as a function of pressure is to split it into contributions from the dimer energy and the cohesive energy: $H_{N_2} = E_{N_2}^{\text{dimer}} + \Delta H_{N_2}^{\text{coh}}$. We note that the dominant contribution to H_{N_2} at ambient conditions is due to the bonding energy of the dimer, which can easily be calculated from first principles. We estimate the enthalpy of cohesion by calculating it for the hexagonal phase at zero temperature and pressure within LDA/GGA and extract the change with pressure using the experimental equation-of-state data [12].

Fig. 3 shows the calculated formation enthalpies within the LDA. For clarity, we consider here only the most important phases; pyrite, baddeleyite, marcasite and the two ST structures. As baddeleyite and marcasite always display similar energies, we have chosen to only include the structure with the lowest formation enthalpy.

We see that for the compounds formed with the group IX and X platinum metals, the ST structures become energetically favored at lower pressures, while the group VIII nitrides form in the marcasite/baddeleyite (MB) structure at all pressures. The range of the stability of the ST structures versus pyrite and MB is consistently pushed towards lower pressures for the group IX nitrides as compared with the group X nitrides.

According to the LDA, the ST structures for PdN₂ and PtN₂ are stable up to 13 GPa, while for IrN₂ and RhN₂ they are only stable at very low pressures. The

high pressure crystal structure of the group X nitrides is that of pyrite, while for all the earlier PM nitrides, the MB structures are the only structures observed at higher pressures.

The same trend is observed in the GGA-calculations, displayed in Fig. 4, except that the relative stabilities of the ST structures are more pronounced as they constitute the low-enthalpy phases up to 20 GPa for PdN₂ and PtN₂ and up to 10 GPa for RhN₂ and IrN₂.

In summary, a consistent feature observed in the phase diagrams is that the marcasite or baddeleyite structures are lowered in energy for the group VIII PM nitrides and the pyrite and ST structures are lowered in energy for the group IX and X PM nitrides

The formation enthalpies reported in Fig. 3 also contain information on the absolute thermodynamic stability of these compounds. According to the LDA all but OsN₂ exhibit at least one stable phase with respect to the separate phases at ambient conditions. In fact, the lowest enthalpy phases for all considered PM-nitrides but OsN₂ are predicted to be stable at all pressures. This is in contrast to the results from the GGA, which predict that the compounds are stable at 12 GPa for RuN₂, 20 GPa for OsN₂, around 15 GPa for RhN₂, IrN₂ and PtN₂ and 25 GPa for PdN₂.

In summary, we find from Fig. 3 the remarkable result that according to the LDA, two novel crystal structures, never observed before, constitute the ground state phases of the group IX and X PM nitrides. Among all these compounds, PtN₂ is the most stable, with a cohesive energy of about 0.3 eV. This is a small driving force for forma-

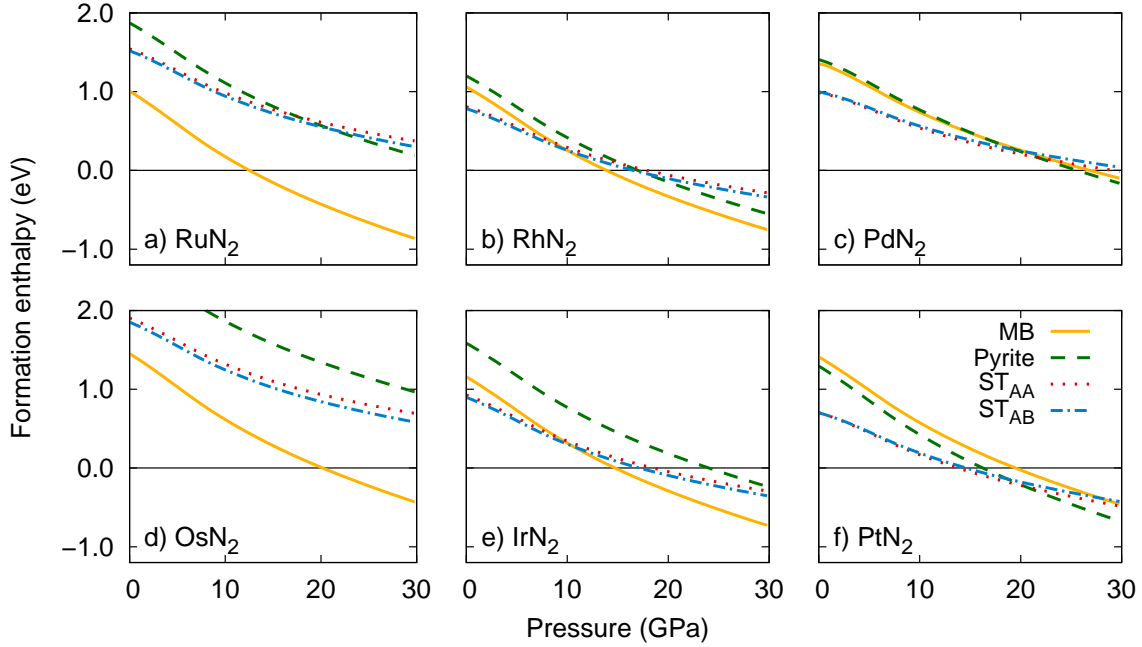


FIG. 4: GGA Formation enthalpies of a) RuN₂, b) RhN₂, c) PdN₂, d) OsN₂, e) IrN₂ and f) PtN₂ as a function of pressure for marcasite or baddeleyite (MB), pyrite and the two simple tetragonal structures.

tion, which may explain why this phase has not been observed in nature. Furthermore, in spite of the agreement between the GGA and the LDA regarding the relative stabilities of the compound structures, GGA predicts all the PM nitrides to phase separate at ambient conditions. For example, according to the GGA, the PtN₂ ST phases are unbound by 0.6 eV at zero pressure, while they become thermodynamically stable between 15-20 GPa. In any case both GGA and LDA consistently predict formation pressures much lower than those observed experimentally even though other calculated quantities and structures are in good agreement with experiment for the nitrides synthesized thus far [3, 7, 8]. For example, the measured synthesis pressure for the nitrides of Pt and Ir is approximately 50 GPa [2, 3], while for palladium nitride it is 58 GPa [5]. Theory does at least predict the order of synthesis pressures correctly for the two group X nitrides. Structures that might form at significantly lower pressures have not been observed by us or reported by other workers. Calculated formation pressures may be low because of kinetic barriers to formation that are not taken into account here. The latter may be associated with for example a strain due to lattice mismatch between the compound and the parent metal on which it is grown. Also the window of pressures over which the enthalpies of formation of the ST structures are both negative and less than those of competing structures may be very small. Careful experimental work at pressures close to known synthesis pressures may be required to produce these compounds. Furthermore, since the associated Raman spectra are probably weak another primary in-situ

diagnostic may be required such as x-ray diffraction.

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